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The principles for an electrochemical digital etching method for compound semiconductors are described and initial results reported. The method is designed to allow atomic level control over the etching process, resulting in the removal of a bilayer of the compound for each cycle. An atomic layer of one element is removed at one potential and then an atomic layer of the second element is removed at a second potential to complete one cycle. The results reported here are for the etching of CdTe. For CdTe, Te is stripped by reduction to Te^{2-} while Cd is stripped by oxidation to Cd^{2+}. Underpotentials are chosen so that only the top atomic layer of an element is removed. Potentials sufficient to strip the element from the bulk of the CdTe substrate are avoided. Application of the method should involve the use of a simple electrochemical cell, with solution convection. The substrate is placed in the cell and a square wave applied, where each cycle results in the dissolution of a bilayer of the compound. The two potentials of the square wave correspond to underpotential stripping potentials for Cd and Te respectively. Directions for the future development of this etching method are discussed.

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DIGITAL ELECTROCHEMICAL ETCHING OF COMPOUND SEMICONDUCTORS

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Abstract

The principles for an electrochemical digital etching method for compound semiconductors are described and initial results reported. The method is designed to allow atomic level control over the etching process, resulting in the removal of a bilayer of the compound for each cycle. An atomic layer of one element is removed at one potential and then an atomic layer of the second element is removed at a second potential to complete one cycle. The results reported here are for the etching of CdTe. For CdTe, Te is stripped by reduction to Te^{2-} while Cd is stripped by oxidation to Cd^{2+}. Underpotentials are chosen so that only the top atomic layer of an element is removed. Potentials sufficient to strip the element from the bulk of the CdTe substrate are avoided. Application of the method should involve the use of a simple electrochemical cell, with solution convection. The substrate is placed in the cell and a square wave applied, where each cycle results in the dissolution of a bilayer of the compound. The two potentials of the square wave correspond to underpotential stripping potentials for Cd and Te respectively. Directions for the future development of this etching method are discussed.

Introduction

The trend towards low dimensional materials in the field of electro-optics has resulted in the need for atomic level control of deposit structure and dimensions. The family of techniques referred to as Atomic Layer Epitaxy (ALE) has arisen to help address that need (1-3). The principle of ALE is that atomic layers of individual elements are deposited sequentially. In this way, layer-by-layer growth (Frank-van der Merwe) is maintained and deposit thickness is controlled by the number of deposition cycles, not by the reactant flux. Our group has been working on the electrochemical analogue of ALE, which we refer to as Electrochemical Atomic Layer Epitaxy (ECALE) (4-6). ECALE is a method for the formation of compound semiconductors where individual elements are alternately electrodeposited at underpotential from separate solutions. The term underpotential (7) refers to the fact that compound formation is generally energetically favorable, compared with formation of bulk deposits of the individual elements. Thus, electrodeposition of one element on a second, forming a surface compound, will frequently occur at a potential prior to (under) that required to deposit the bulk element. Deposition is surface limited: limited to an atomic layer, as diffusion of the depositing element into the substrate is generally a slow process at room temperature.

In addition to atomic control over deposition, atomic control over material removal is desirable. Digital etching is just beginning to emerge as an active area of research (i). Present attempts at digital etching involve cycles where a reactant gas is first adsorbed on the substrate surface and then a reaction is initiated using an energetic beam of electrons (i1), ions (i2) or photons. Reaction of the monolayer of adsorbed gas occurs only with the surface, forming a volatile compound, and thereby removing one atomic layer of the substrate. Etching involves the application of this cycle. Digital etching appears to be applicable to elemental semiconductors (i4), compound semiconductors (i5) and other materials such as metals and insulators.

Whereas the above studies involved a single etchant gas and a subsequent reaction initiation (8-12), ALE of compound semiconductors involves the use of different reactant precursors for the deposition of the individual elements (1-3). This suggests scenarios for digital etching of compound semiconductors where atomic layers of each of the component elements are removed preferentially using separate etchant species, leaving an atomic layer of the other element. The present paper describes some preliminary studies of the feasibility of performing digital etching electrochemically on compound semiconductors where electrons are used to remove an atomic layer of one element, and holes are used to remove an atomic layer of the other. This process is a natural outgrowth of ECALE, as again, the underpotentials for the component elements are used (although, in the digital etching process a single electrolyte solution is used, containing no precursors to the substrate's component elements).

Figure 1 is a diagram indicating the potentials for the decomposition of CdTe and the species formed in aqueous solutions as a function of pH. It is essentially a Pourbaix diagram (j). The shaded region of the diagram indicates areas where CdTe is stable. The initial decomposition of CdTe at positive potentials results in loss of Cd as a Cd^{+2} species, dependent on the solution pH, while decomposition at negative potentials results in the formation of telluride ion. The hatched regions in the diagram represent the difference between the potentials for dissolution of the bulk element and decomposition of CdTe. The hatched regions in essence represent the underpotentials for the elements.

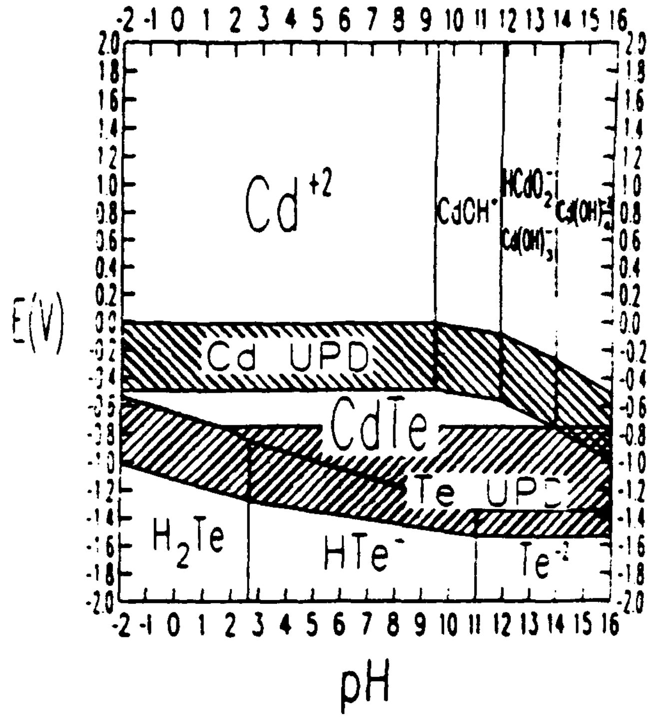

Figure 1. Pourbaix diagram describing the decomposition of CdTe.

The diagram in Figure 1 has been drawn assuming an activity of 1 for the CdTe and 10^{-3} M for all soluble species. All potentials in the diagram are vs the SHE reference electrode. These conditions are most applicable for a stoichiometric surface and a fairly concentrated layer of solution in contact with the electrode surface. Given a stoichiometric surface, the digital etching process can begin by dissolution either of Cd or Te. If we start with dissolution of Cd, selection of a potential in the upper hatched region of Figure 1 will result in dissolution of Cd bulk but not Cd present in CdTe. By choosing a Cd stripping potential closer to the CdTe stripping line (a more positive potential) more Cd will be depleted from the CdTe surface. Potential selection for the stripping of Cd is a critical step in optimizing the digital etching process. Ideally, the potential will be selected sufficiently close to the upper CdTe decomposition potential to result in removal of the top atomic layer of Cd, leaving a full atomic layer of Te. No further Cd removal should occur as the remaining Cd atoms are bound to Te atoms. The Te stripping potential would then be selected close to the lower CdTe decomposition potential in order to remove the Te atomic layer, leaving a Cd atomic layer.. No further Te removal should occur as the remaining Te atoms are bound to Cd atoms.

Digital electrochemical etching of CdTe involves applying a square wave where one potential is selected sufficiently negative so as to reduce the top layer of Te atoms, yet positive enough that Te atoms are not stripped from sites that have a full complement of Cd bonds. The other potential is selected sufficiently positive to oxidize the top atomic layer of Cd atoms, yet negative enough so that Cd atoms that have a full complement of Te bonds do not strip out. Etching then consists of application of this square wave with a period long enough for complete dissolution of the respective elements. Active mass transfer (flow of the electrolyte over the surface) will be applied in order to remove the product ions. Each cycle ideally removes a single CdTe bilayer. This square wave period is a function of the kinetics of the dissolution reaction and the rate of electrolyte flow. If the flow is too slow, some ions, still in the diffuse layer, will redeposit with the change in potential in the subsequent half cycle.

Experimental

For the studies presented here a thin layer electrochemical cell (TLE) was used, as it allowed better quantification of the dissolved amounts. It is not our contention that the TLE is the best electrochemical configuration for this procedure, only that it is a good design for the present studies. Figure 2 is a schematic drawing of the experimental setup. The TLE consisted of a CdTe single crystal (II-IV Inc.) sandwiched between a piece of Au foil and a teflon gasket. On top of the Teflon gasket was a Plexiglass plate. Contact to the CdTe crystal was made using an In contact, annealed on the back side. Electrical contact to the In was made by pressing it against the Au foil.

An ellipse cut in the Teflon gasket served as a channel for the flow of electrolyte. The electrolyte solution was delivered from a pressurized Pyrex bottle through the Plexiglass plate of the cell. The flow rate was controlled using the gas pressure and a needle valve on the outlet of the solution reservoir. Flow through the cell was turned on and off using valves at the entrance and exit to the cell. By stopping the flow, the amounts of ionic species produced in the various etching steps could be investigated coulometrically. That is, once stripped, Cd^{+2} or Te^{2-} could then be quantified from their subsequent redeposition. Alternatively, the resulting ions could be quantitatively removed by flushing the cell with the electrolyte solution. To etch the surface, the electrolyte would be kept flowing; stopping flow was only performed in the present studies for analytical purposes.

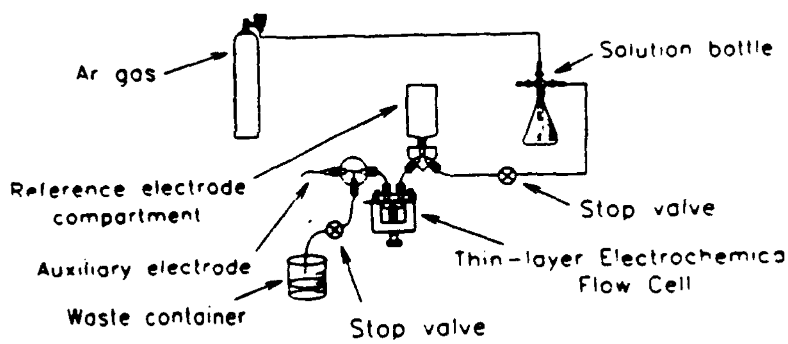

Figure 2. Diagram of the thin-layer electrochemical flow cell.

Results

Initial pretreatment consisted of a 1% Br-methanol etch of the sample, as received from II-VI Inc.. As described in a previous article (14), the Br-methanol etch results in preferential etching of the Cd and leaves a thin layer of elemental Te on the surface of the CdTe. The Te layer was subsequently removed by electrochemical reduction to telluride ion. The surfaces resulting from this procedure have the simple unreconstructed structure, in the case of the (111) planes of CdTe. That is, simple (1X1) LEED patterns were previously observed on both the A and B faces of a CdTe(111) single crystal after etching and the electrochemical reduction of excess Te (14). Alternative pretreatments, such as ion bombardment followed by annealing, generally result in reconstructed or nonstoichiometric surfaces.

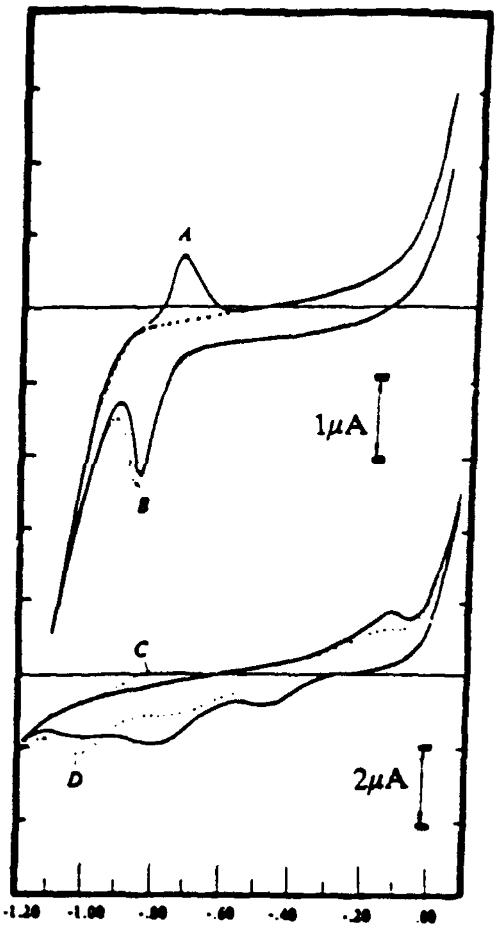

Figure 3. Voltammetry of a CdTe single crystal. Solution composition was 0.01 M $Na_2B_4O_7$ and 0.5 M Na_2SO_4. The scans were all run at 5 mV/sec.

Figure 3 is a series of voltammograms taken with the TLE flow cell depicted in Figure 2. The voltages shown in Figure 3 are referenced to the Ag/AgCl (1 M NaCl) reference electrode. Figure 3a was run on the clean CdTe crystal, starting at 0.0V. This initial potential is sufficient to oxidize multiple atomic layers of Cd. The removal of multiple layers of Cd results in formation of several layers of bulk Te. This was done in Figures 3a and 3b to accentuate the Te stripping features. To remove the Cd^{+2} ions formed at potentials above -0.2V, the initial part of the scan was run with the electrolyte flowing. At -0.2V the flow was stopped. The absence of any reduct-ion peaks until -0.9V indicates that all the Cd^{+2} ions were quantitatively removed. The reduction peak for Te to Te^{-2} (-0.9V) and the subsequent oxidation peak for Te^{-2} to Te (-0.8V), in the positive going scan, are clearly evident in Figure 3a. As mentioned above, the size of the peaks are a function of the amount of Cd stripped at potentials above -0.2V. In this case, approximately 5 atomic layers of Cd had been removed and this is reflected in the size of the resulting Te stripping. Figure 3b was run right after 3a and differs only in that the TLE cavity was rinsed continuously during the negative going scan, until the direction was changed at -1.1V. This resulted in the removal of all Te^{2-} ions formed. The subsequent Te^{2-} oxidation (-0.8V) was thus absent from the positive going scan. Experiments where the positive going scan was subsequently reversed at -0.5V and scanned back through -0.9V indicated no significant Te reduction. Only Te from which the Cd has been stripped (at potentials above -0.2V) could be reduced at -0.9V, and that Te^{2-} had been previously removed during the initial reductive scan with the solution flowing. Subsequent Te reduction would require a still more negative potential, as the remaining Te was stabilized by bonds to Cd. The reduction current observed negative of -1.0V (Figure 3) is due mostly to the hydrogen evolution reaction at this pH. The hydrogen evolution reaction depolarizes the electrode, limiting further Te reduction.

The lower two cycles, Figures 3c and 3d, illustrate the Cd dissolution reaction. Figure 3c involved the initial dissolution of Cd at potentials in excess of 0.0V. The solution was kept flowing until -0.28V, so that Cd^{2+} ions would be flushed from the cell. The Te reduction process at -1.0V and the subsequent Te^{2-} oxidation peak are both present in Figure 3c (the changes in peak positions are probably the result of contact resistance changes from 3a and 3b, and changes in the IR drop in the TLE cavity, as 3c and 3d were run with a different CdTe sample.) A small peak at -0.1V on the subsequent oxidative scan is visible as well and corresponds to the dissolution of bulk Cd: Cd not stabilized by the presence of Te. In Figure 3d the Cd^{2+} produced during the oxidative scan was not rinsed from the cavity and thus its rereduction is visible in two peaks at -0.5V and -0.8V. The first Cd^{2+} reduction peak is due to UPD, or the deposition of Cd^{2+} on the exposed Te. The second peak is due to deposition of bulk Cd and its size is a function of the amount of Cd^{+2} formed at anodic potentials. A small amount of Te reduction is also visible at -1.0V, but as most of the Te was covered by the depositing Cd, the peak is considerably smaller than the equivalent scan, Figure 3c, where all the Cd^{+2} was rinsed away. The cell was rinsed with electrolyte at -1.2V (Figure 3d) to remove any Te^{2-} formed and the absence of the Te^{2-} oxidation peak at -0.8 is clear. The size of the Cd^{2+} reduction feature in Figure 3d at -0.8V indicates that a significant amount of bulk Cd was formed on the surface and this is reflected in the subsequent oxidation feature at -0.1V. The increase in the size of this peak, over that in Figure 3c, indicates the increased bulk Cd coverage.

Discussion

The results reported above indicate that the concept of UPD can be applied here to the stripping of atomic layers of individual elements. Both for the reduction of Te to form Te^{2-} and for the oxidation of Cd to form Cd^{2+}, significantly different potentials are required to strip the bulk elements relative to the elements present in the form of the compound. By careful selection of stripping potentials, it should be possible to remove only the top atomic layer of a given element. From the results in Figure 3 it appears that a potential near -1.0V could be used to strip an atomic layer of Te, while a potential near -0.1V would be used to strip an atomic layer of Cd.

The voltammetry in the experiments reported above was not optimal. Several problems were apparent in the experimental setup. The most critical appears to be the formation of an adequate ohmic contact to the CdTe. Other problems, specific to the flow cell design, include variations in the cell's IR drop and trapping of electrolyte under the Teflon gasket. The extent to which electrolyte is trapped appears variable in the present studies. It can be minimized by tightening the cell more, although this increases the probability that the fragile CdTe substrates will crack. The main drawback to the trapped electrolyte volume is the increased charging current associated with the electrochemical double-layer. It appears that the contributions to the observed faradaic processes are minimal, as the IR drop in the very thin trapped layer of solution is exceedingly large and mass transfer is negligible.

The optimal cell configuration for electrochemical digital etching appears to be a thick layer cell, good convection, or a hydrodynamic cell where the electrolyte is continuously exchanged. The complexities of the TLE design and operation would be avoided.

Other problems to be addressed include whether to etch in the dark or with light present. Significant changes are observed in the background currents with the introduction of light. Continuing work on the etching conditions will be performed without light, until more is known about the optimal etch conditions. As well, the pH of the solution used here, pH 9, may have been too high. It was selected so that the hydrogen evolution reaction would not interfere with characterization of the Te reduction reaction. Problems associated with the Cd stripping reaction may have been due to the facile formation of $Cd(OH)_2$ at pH 9 (k_{sp}=5.9X10^{-15}). Although the amount of Cd^{2+} is quite small, the concentration is probably sufficient to initially cause formation of the hydroxide in the diffuse layer. Solutions buffered to lower pH values will be investigated in future studies.

The dependence of the etching process on the nature of the CdTe substrate is not clear. Two crystallographic planes were examined, the (111) and the (100). There may be significant differences in the reactivities between the two surfaces, but due to the variables described above, no conclusions may be drawn at this time. Investigations into the substrate dependence, in the future, will need to include control over the surface crystallography of the substrate and the dopant density and carrier type.

The digital electrochemical etching of compound semiconductors appears to be workable. The ease with which potentials can be changed makes electrochemistry very attractive for digital control over the etching process. That is, exchange of one etched species, electrons, for another, holes, is fast and complete.

A number of important variables still need to be considered and investigated, including: the stripping potentials; stripping times (a function of the dissolution kinetics and fluid flow); solution composition and pH; cell design; and substrate structure and doping. The present experiments were performed on CdTe in an aqueous solution. It is probable that other compounds should work as well, such as GaAs etc.. Further, the use of nonaqueous etch solutions will have advantages where relatively negative potentials are required, in order to avoid interference from the hydrogen evolution reaction.

Acknowledgments

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